論　文　の　要　旨

題目　Gasification of lignocellulosic biomass under sub- and super critical water condition: Interaction between model compounds and process evaluation
（亜臨界及び超臨界水中におけるリグノセルロース系バイオマスのガス化: モデル物質間の相互作用およびプロセスの評価）

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Biomass derived energy is one promising candidate to substitute depleting fossil fuel. Due to that most of biomass resources come as wet form, supercritical water gasification (SCWG) is promising method to convert biomass into gaseous products because water is considered as reactant in the process hence there is no need to dry the biomass beforehand. Supercritical water is the water at fluid phase when temperature is above its critical point (374 °C, 22.1 MPa). At this state, water has high potential as a solvent for organic components and gases. As a result, biomass could be homogeneously dissolved in supercritical water and consequently obtain high conversion. However, biomass consists of various compounds that make difficulty to optimize the process. Thereby, reaction scheme and model compound of biomass are keys to achieve the goal. For lignocellulosic biomass, it contains mostly cellulose, hemicellulose and merged by lignin.

According to that only few studies have been investigated in behavior of hemicellulose in supercritical water, this study firstly attempts to elucidate the decomposition of xylose as a model compound of hemicellulose in supercritical water aiming for comprehending the whole behavior of lignocellulosic biomass. Solutions of xylose in water were heated under sub- and supercritical conditions in the temperature range 350－450 °C in a continuous reactor at a controlled pressure of 25 MPa. Kinetic analysis of xylose in subcritical water in comparison to supercritical water was conducted. The reaction network was proposed, which is mainly included of isomerization, dehydration and retro-aldol condensation. The major species of liquid intermediates were furfural, which is the dehydration product of xylose, retro aldol products, and organic acids. Under the critical point of water, xylose dehydration is favored. In contrary, retro aldol condensation is favored when the water temperature is above the critical point. Two organic acids were found significant in the decomposition products. First, formic acid is known to be the final precursor for the gasification that produce hydrogen and carbon dioxide through decarboxylation. The other abundant organic acid was acetic acid. Unlike formic acid, acetic acid was stable in supercritical water and rarely gasified. In addition, the effect of temperature was used for the classification of the reaction types. The temperature shift from subcritical to supercritical region affected the properties of water, specifically ion products. Therefore, ionic reactions were suppressed in supercritical conditions, whereas radical reactions were not affected by the change in the property of water. This criteria was considered in order to categorize the ionic reactions and radical reactions taking into account of Arrhenius behavior. In summary, dehydration did not obey Arrhenius behavior and concluded as the ionic reaction. Retro aldol condensation and gasification, in contrast, followed Arrhenius behavior and concluded as the ionic reactions.

Consequently, the interaction between model compounds of lignocellulosic biomass, which are glucose, xylose and guaiacol as a model compounds of cellulose, hemicellulose and lignin respectively,

is studied. Gaseous, liquid and solid products were collected and quantitatively determined. Liquid product is dominant in the range of this work. Intermediates that are of focus were glucose, fructose, 5-HMF, furfural, xylose, xylulose, retro-aldol products, acids, guaiacol, and phenolic compounds. Interaction of these intermediates had an effect on kinetics of reactions and distribution of the final products. The reaction pathway of three model compounds is developed and proposed in this study. Interestingly, some radical reactions that were supposed to be enhanced in supercritical condition was suppressed. Similar results happened to char formation from guaiacol, which proceeds also through radical reactions. This indicated the radical scavenging effect that may generate from some intermediate compounds, such as, formic acid, acetic acid, and phenolic compounds. These compounds provided various types of radical, thus possibly affected intermediate reactions differently. Nevertheless, gasification was not influenced by such an effect.

The decomposition of glucose was employed for the consequent study because both most of the intermediate reactions in the reaction network are ionic reactions except gasification, which is radical reaction. As such, phenol was expected to inhibit gasification as a result of the radical scavenging effect. The kinetic analysis was conducted in order to investigate any changes in reaction kinetics. The results indicated that char formation was enhanced in subcritical condition, whereas no significant difference in supercritical condition in a presence of phenol. Because char formation from glucose was found as ionic reaction, it can be implied from this result that phenol could also act as acidic catalyst in subcritical condition. Gasification, which is a radical reaction, was suppressed in both sub- and supercritical condition, which indicated that phenol may also contribute to the radical scavenging effect.

At last, process evaluation of supercritical water gasification of biomass in Kita-Hiroshima town, as an outcome of the on-site team project conducted under the requirement of Taoyaka program is presented. During the visit to Kita-Hiroshima, it was found that the Japanese rural area is facing serious depopulation. On the other side, there is a large potential in agriculture that can attribute to resilience and independence of the area. Therefore, tomato was chosen as a study case for the implementation of technology for creation of a value-added product and conversion of waste to energy aiming at the least dependency of the town to the other outsources. SCWG, as mentioned to be suitable for wet biomass, was taken into an account for the conversion of tomato residue. The SCWG process design and products determination were carried out attempting the best energy efficiency by applying the heat exchanging network. As a result, the energy produced is 5.8 MJ/kg from SCWG of tomato residues feedstock. This amount of energy was utilized as heat supplying to the dried tomato processing and the greenhouses. Therefore, an income from selling dried tomato as a value-added product was generated. In addition, the profit was maximized by the utilization of energy from the residue. It was proved that the utilization of the SCWG of tomato residue helped reducing carbon oxide emission as well. Therefore, the evaluation suggested that SCWG of tomato residue in Kita-Hiroshima is effective in perspective of energy, economics, and environment.

In conclusion, this research includes fundamental studies, which elucidates mechanisms of model compounds of lignocellulosic biomass in terms of kinetic analysis. These fundamental studies are essential for applying SCWG of biomass in practical way because difference in biomass content is important key to consider for its conversion into energy or desirable chemical compounds. A detailed kinetics study allow ones to predict the outcome of the reactions. Furthermore, practical utilization of SCWG system was evaluated to reveal its feasibility in terms of energy, economic and environmental viewpoints.